# Disordered Rocksalt Transition-Metal Oxides (TMOs): High voltage and surface issues

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*This poster specifically describes the work on surface studies and high voltage electrolyte/cathode processes, and is an addendum to poster BATT376*

Project ID: bat376_part2

# Overview

## Timeline

- Start date: October 2018
- End date: September 2021
- Percent complete: 50%

## Budget

- Total project funding
  - FY19 $1.9 M (LBNL+UCSB only)
  - FY20 $1.135 M (LBNL+UCSB only)
- BAT376, BAT404, BAT405 and BAT406 (LBNL, ORNL, PNNL, UCSB)

## Barriers Addressed

- Energy density
- Cycle life
- Cost

## Partners

- Lawrence Berkeley National Laboratory
- Oak Ridge National laboratory
- Pacific Northwest National Laboratory
- UC Santa Barbara

# Relevance/Objectives

- Cathode materials based on cation-disordered Li-excess rocksalts (DRX) can deliver energy densities up to 1000 Wh/Kg and > 3000Wh/l (cathode only)
- DRX structure allows a wide range of chemistry, providing an opportunity to develop Co-free high energy density cathode materials that are alternative to the traditional layered NMC-type cathodes. In particular materials with Mn-redox are being investigated.
- Fundamental understandings on what controls DRX performance characteristics, particularly rate capability, cycling stability and voltage slope, are key to enabling rational decisions on further development of this newer class of cathode materials.

*This poster specifically describes the work on surface studies and high voltage electrolyte/cathode processes, and is an addendum to poster BATT376*

# Milestones

| Date | Milestones | Status |
|---|---|---|
| December 2019 | Obtain information on particle morphology as function of fluorine content to understand which surfaces are exposed. | Completed |
| March 2020 | Characterization of short range order in multiple DRX materials and relation to performance | Completed |
| June 2020 | Modeling of percolation and Li transport in at least two fluorinated DRX compositions | On schedule |
| September 2020 | Obtain spectroscopic information on at least two DRX compositions to determine redox behavior and distinguish metal redox from anion redox.  Correlate to performance | On schedule |

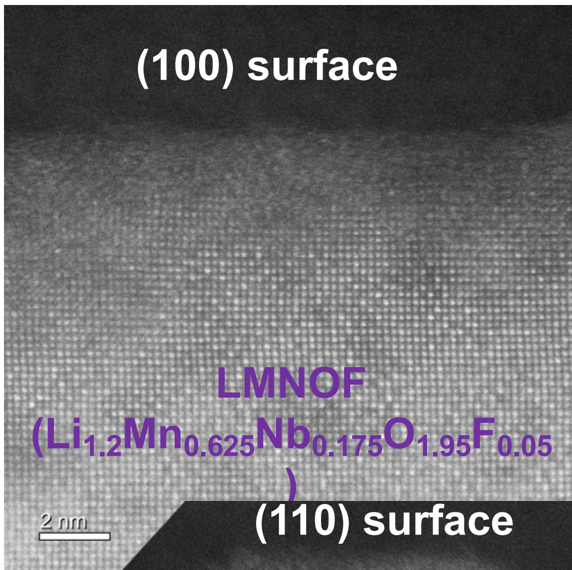
# Approach

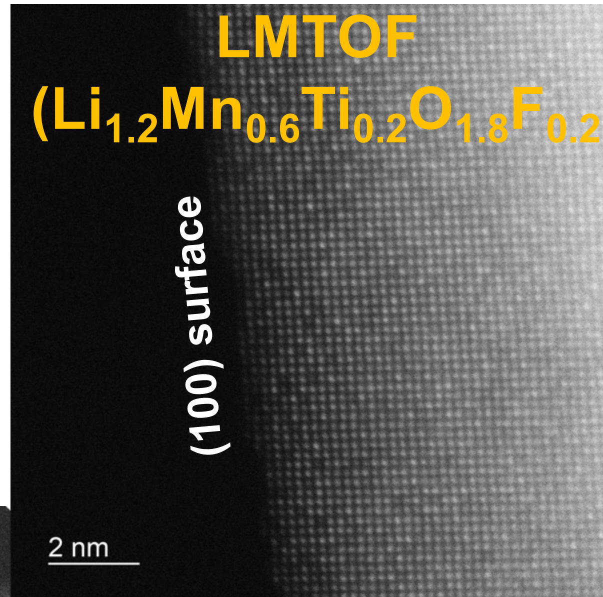
- Focus on three DRX baseline systems and their analogues:
  - $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF): Solid-state synthesis, Mn-redox
  - $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$(LNTMOF): Solid-state synthesis, Ni-redox
  - $Li_2Mn_{1/2}Ti_{1/2}O_2F$ (LMTOF): High F-content, ball-milled, $Mn^{2+}/^{4+}$ redox
- Modeling of surface facets, possible segregation to them, and stability of them against O-loss with and without fluorine substitution
- XAS before and after cycling to characterize the surface species
- DEMS to evaluate O-loss for samples with and without F substituted
- Chemical titration to evaluate carbonate content on surface
- TEM to evaluate surface structure before and after cycling
- Measuring F-content in electrolyte as function of cycling using salts and binders with and without F to separate source of F.
- In-operando Raman spectroscopy to detect complex surface species after cycling
- NMR to detect surface and bulk changes

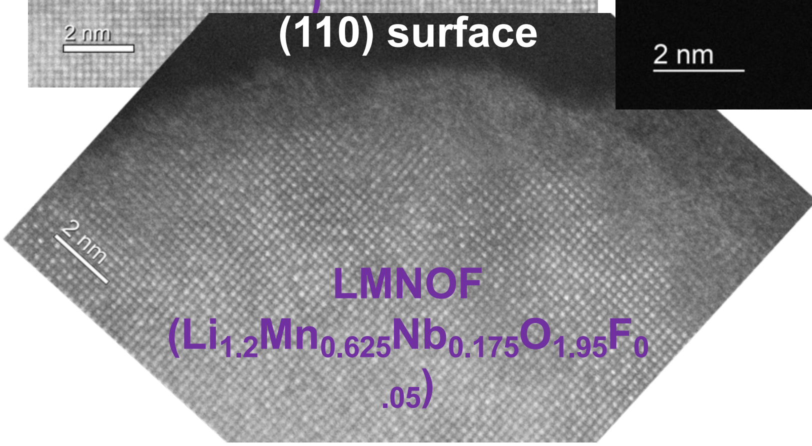
# Surface facets and structural features of $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF) and $Li_{1.2}Mn_{0.6}Ti_{0.2}O_{1.8}F_{0.2}$ (LMTOF)

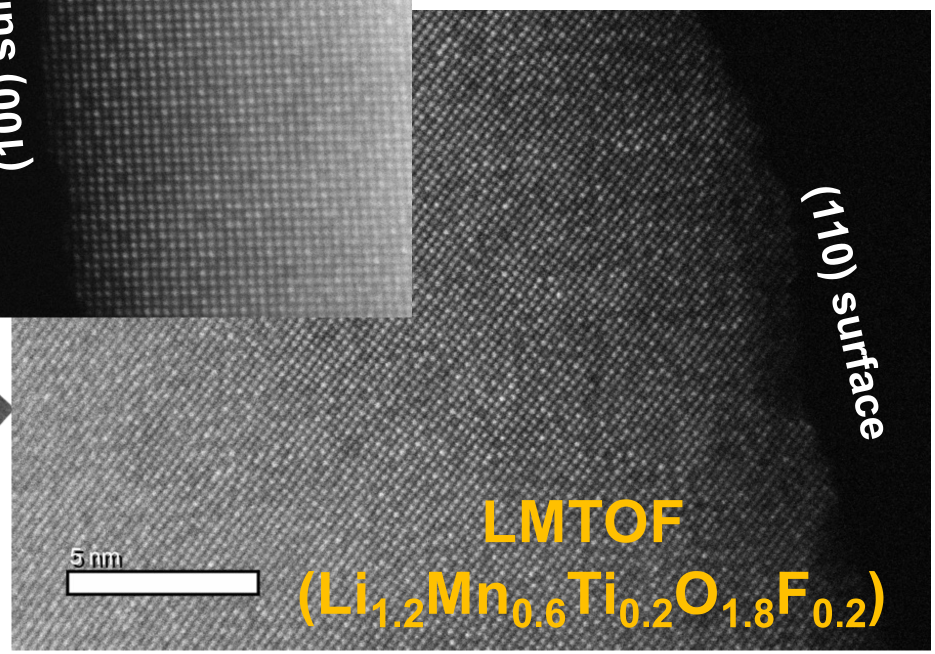
**Key message:**

- Surfaces of LMTOF are clean and show sharp crystalline lattice termination;
- Surfaces of LMNOF are covered by a ~2 nm amorphous layer.
  - LiF, $Li_2CO_3$?
- Surface facets correspond to (110) and (100)

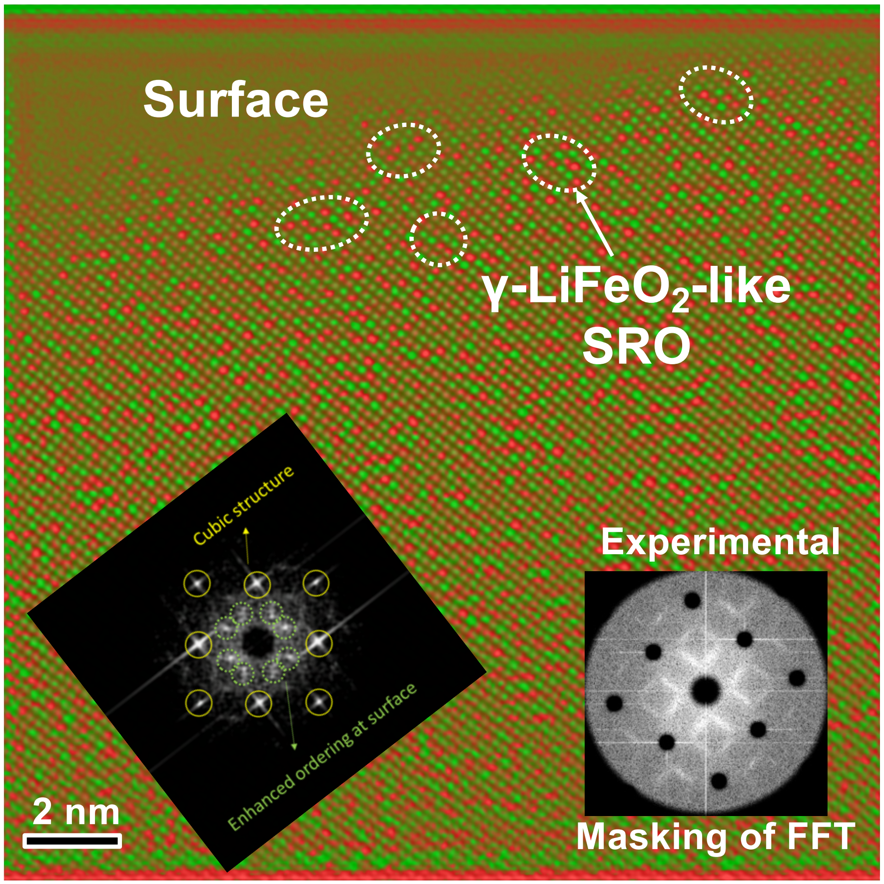


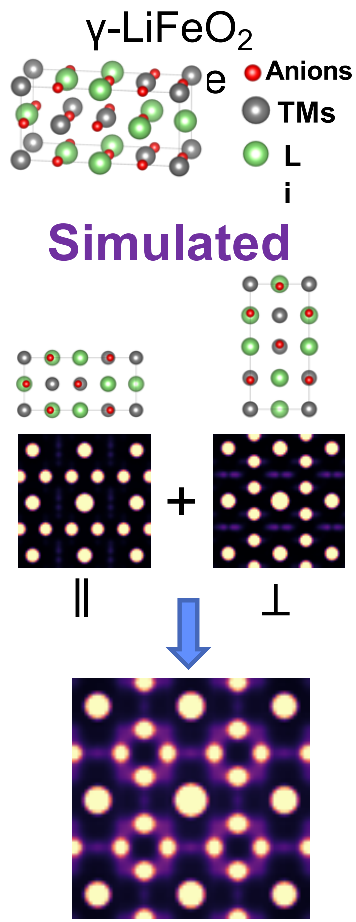



# Direct visualization of atomic-scale ordering enhancement at surfaces of LMTOF through image filtering



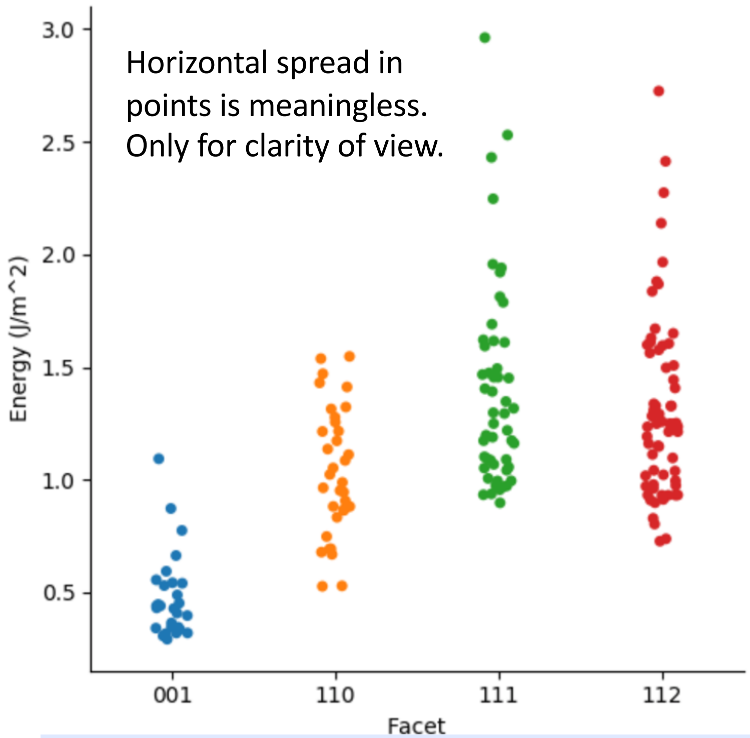

Filtered image excluding cubic lattice information



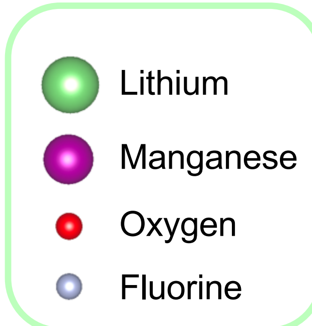

**Key message:**

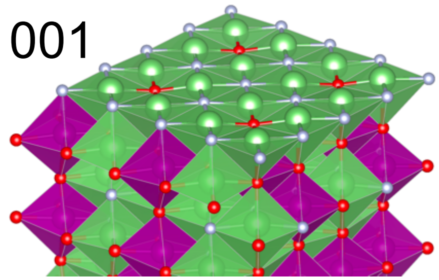
- FFT of the STEM-HAADF shows both diffraction spots of rocksalt phase and diffuse scattering
- Filtering of the image reveals the spatial variation of the short-range ordering
- Enhanced ordering occurring at the surface is due to formation of local γ-LiFeO2-like SRO regions.

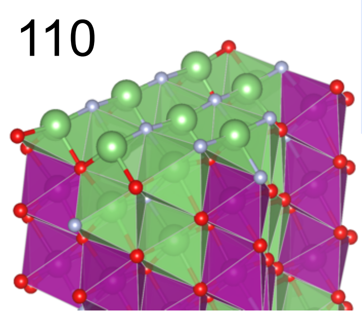
# Modeling: $Li_2MnO_2F$ low energy surfaces and equilibrium particle shape



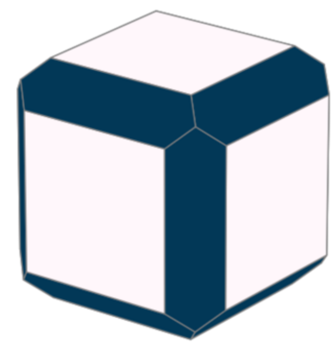

Surface energy of facets with a variety of surface decorations and segregation. 001 and 110 are lowest, in agreement with TEM observation

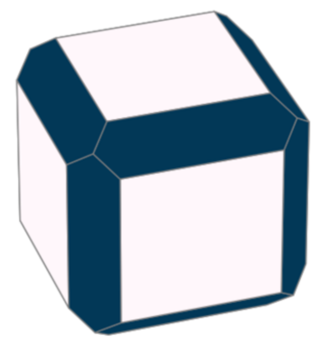



Low energy surface structures have **some Li and F segregation**

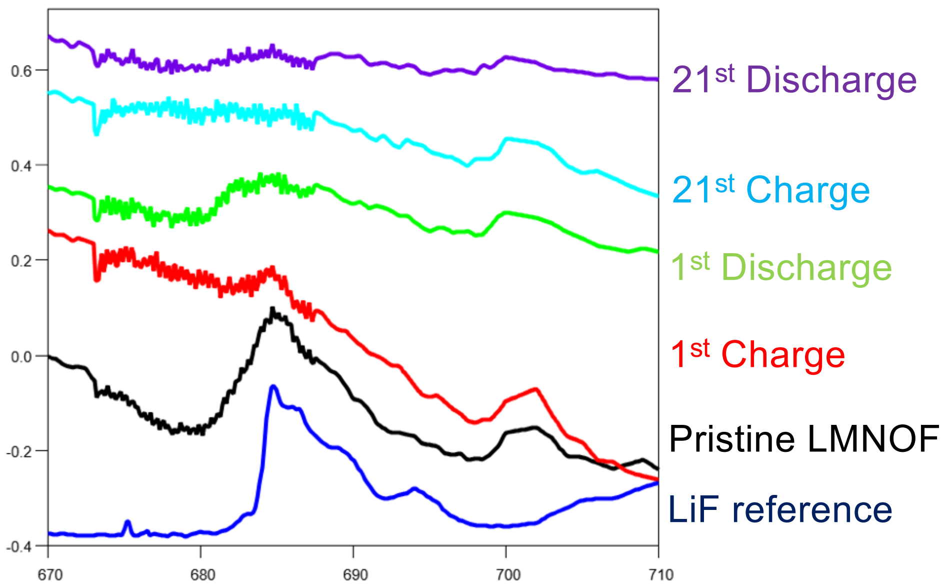





# Tracking Fluoride on surface of LMNOF

- Likely LiF, not transition metal fluoride; very small amount (~1%) of total F in LMNOF on surface
- Surface F content vanishes upon cycling with F free electrolyte/binder. Not clear yet whether F truly “disappears” from surface or whether it gets buried by other decomp products

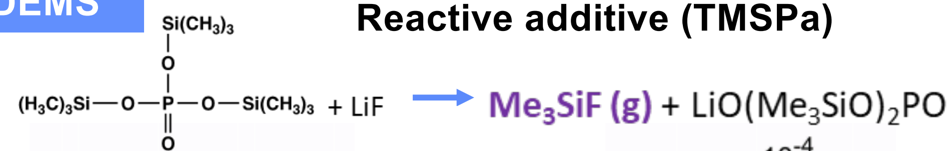
**XAS**

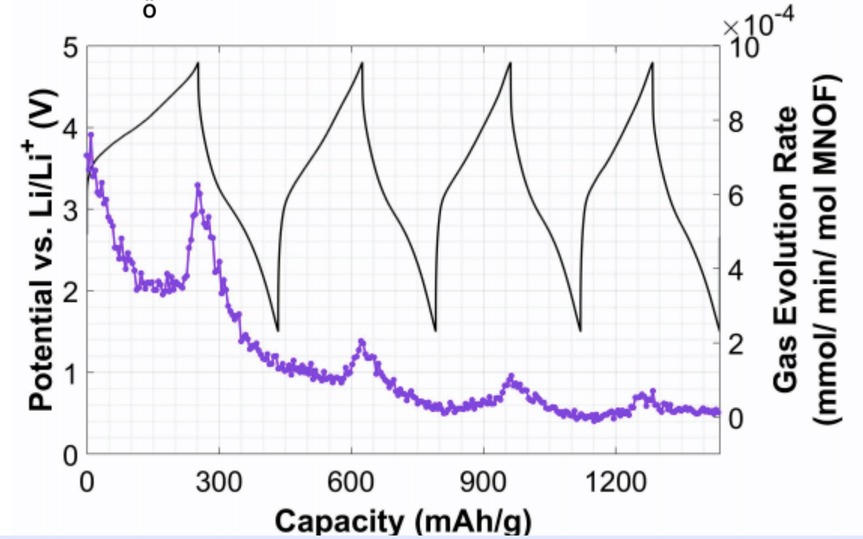



F K-edge XAS for surface shows disappearance of F signal with cycling.

**DEMS**

**Reactive additive (TMSPa)**




Using a F-scavenger in the electrolyte we can measure the amount of F dissolved.

In these experiments a polyethylene binder and $LiClO_4$ salt are used to prevent any interference from other F-sources

# *Ex situ* ATR FTIR of Cycled $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ Electrodes

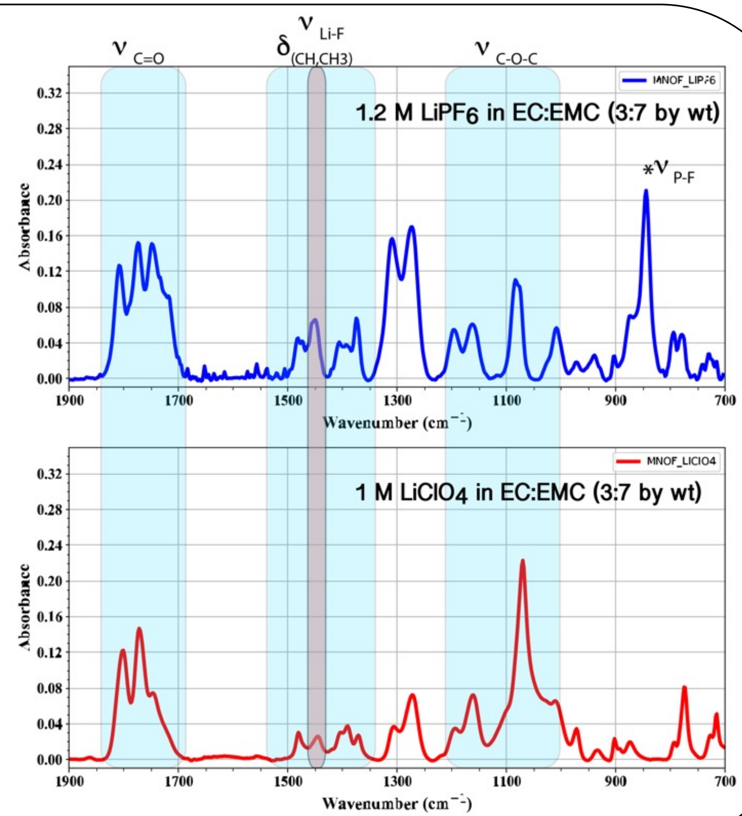
•Spectra were recorded after two cycles at C/20 between 1.5 and 4.8 V (no washing):

1. 1 M $LiClO_4$ in EC:EMC
2. 1.2 M $LiPF_6$ in EC:EMC

•FTIR spectra reveal LiF at the surface of the cycled LMNO DRX electrodes.

➢ Possible source(s):

1. $LiPF_6$
2. DRX
3. PTFE






To separate the possible sources of F at the surface or in the electrolyte, tests with F-free salt and binder were prepared

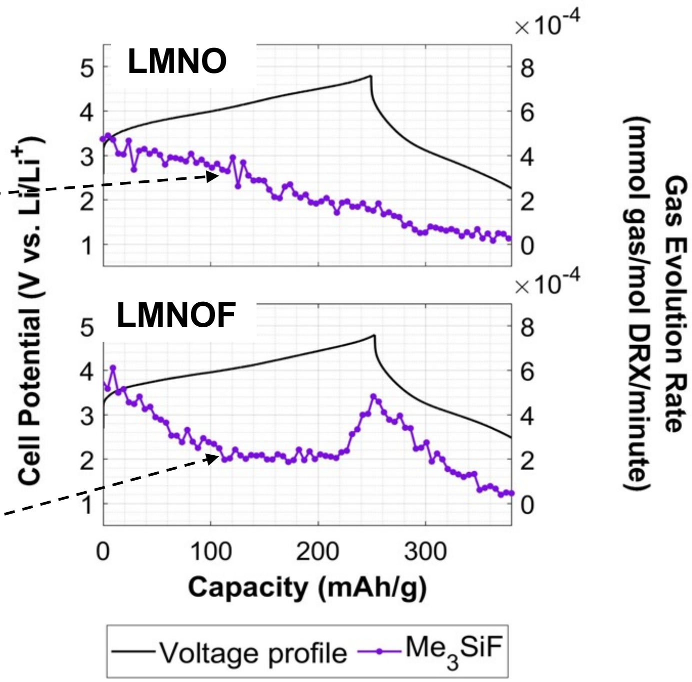
# DEMS: Origins of Fluorine-containing Compounds is LiPF6

•2nd cycle in 1M $LiClO_4$ , EC/DEC
+ 1% TMSPa, PE binder

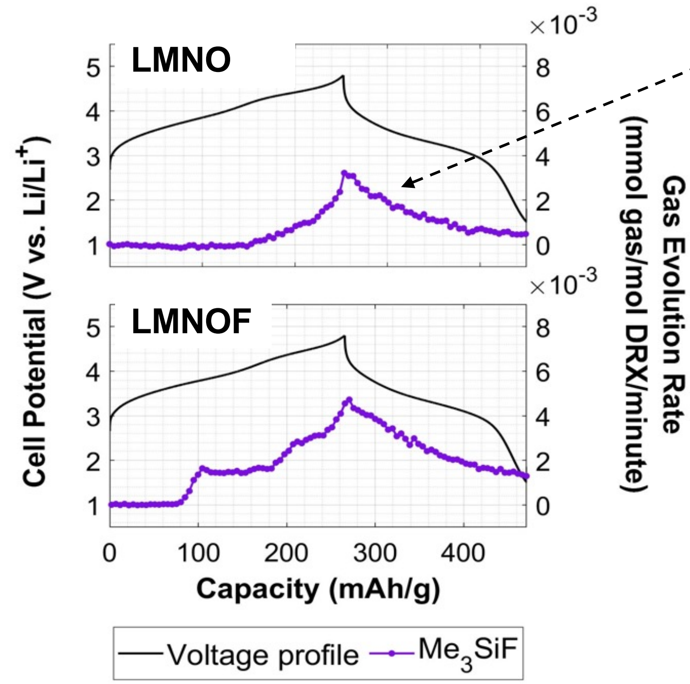
2nd cycle in 1M $LiPF_6$, EC/DEC
+ 1% TMSPa, PE binder

Baseline for amount of F in electrolyte

Only very small amount of F in electrolyte when charging F-DRX

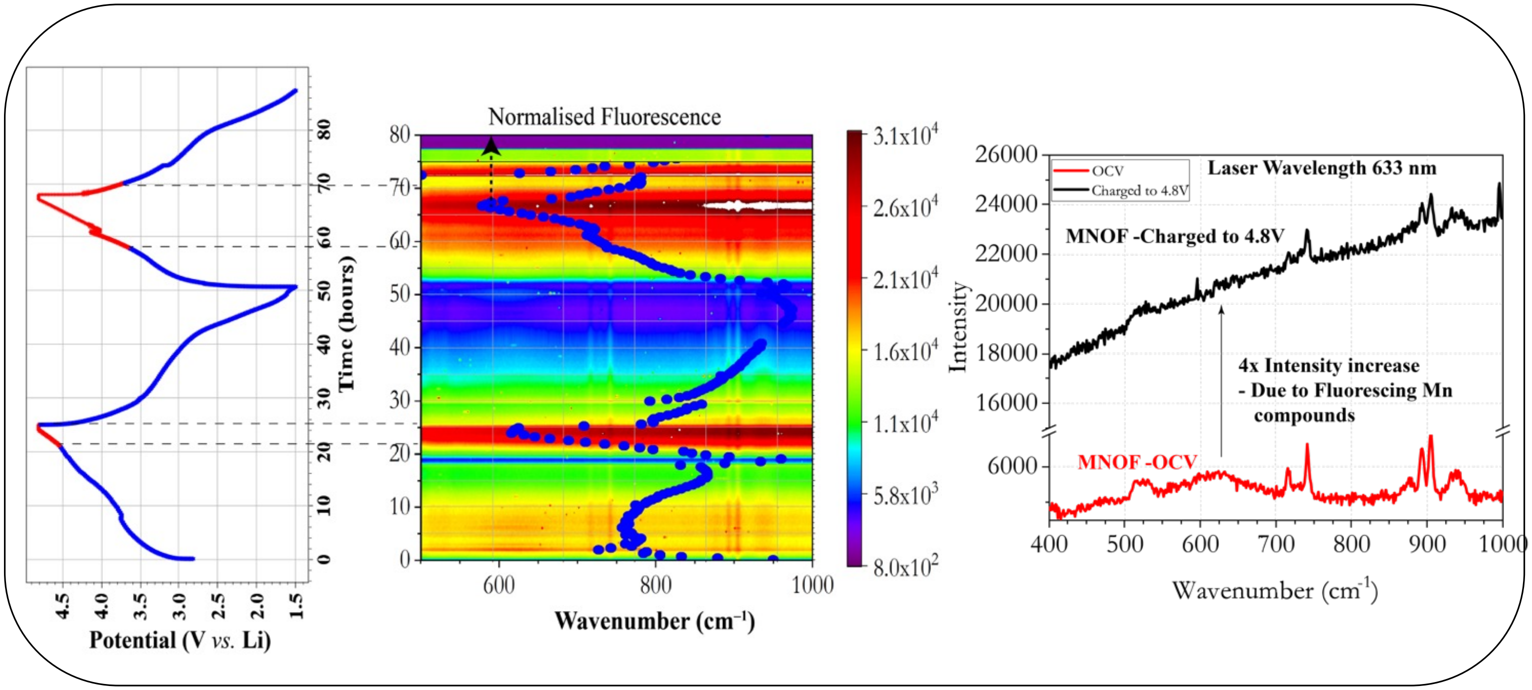



Much larger F amount in electrolyte when using LiPF6




- $LiPF_6$ is the main source of fluorine released at DRX and F-DRX cathodes
- F-DRX lose small amounts of F but it seems to accelerate $LiPF_6$ decomposition

# *Operando* Raman of $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$

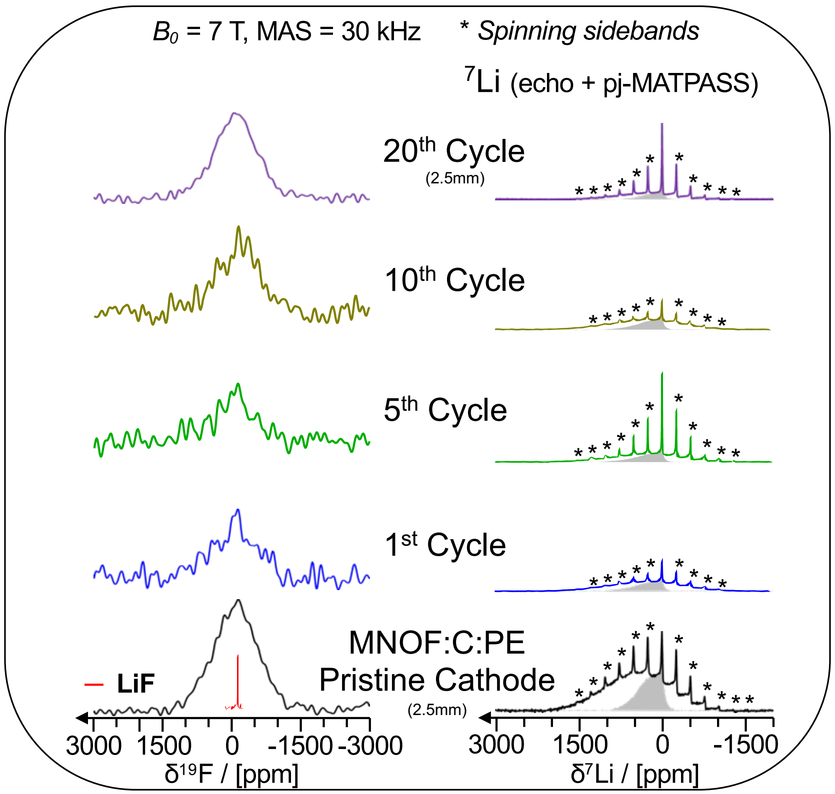


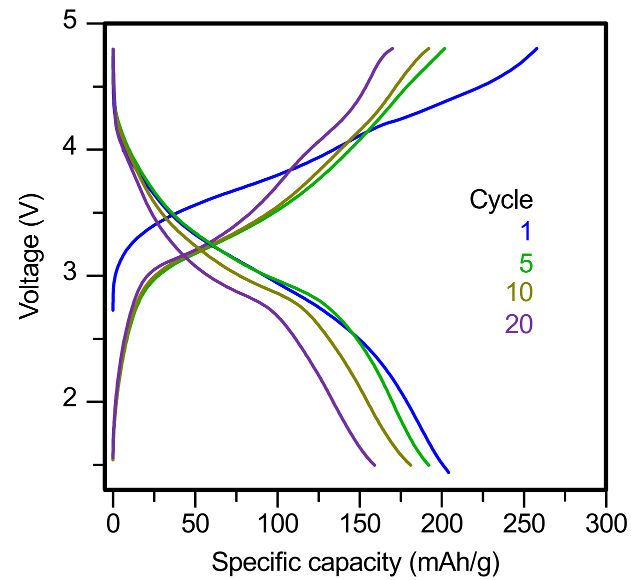

- High-intensity fluorescence emission at potentials >4.5 V
- Fluorescent products tend to accumulate on the surface with cycling
- TMs from the surface reacting with electrolyte solvent forming $Me^{(II)}$ bis-acetylacetonate and $Me^{(III)}$ tris-acetylacetonate

Jarry et al., JACS 2015, 137, 3533

# $^{19}F$, $^{7}Li$ NMR of Cycled F-DRX Electrodes

LiMNOF (no carbon additive, F-free PE binder) cycled in 1M $LiClO_4$ in EC:DEC at C/20 between 1.5-4.8 V, discharged to 1.5 V, washed in DMC prior to analysis

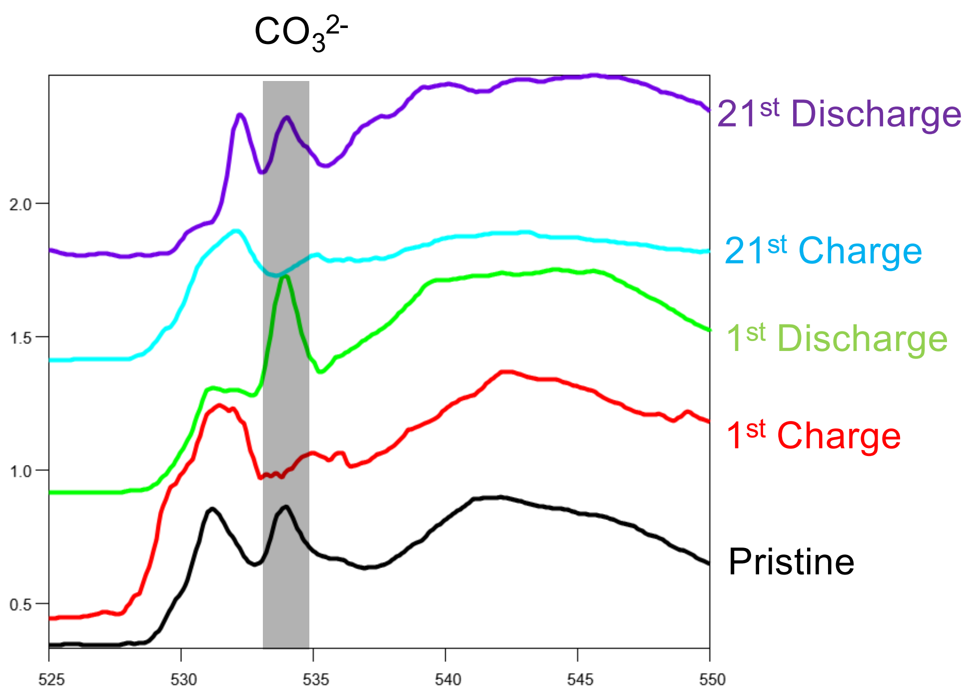


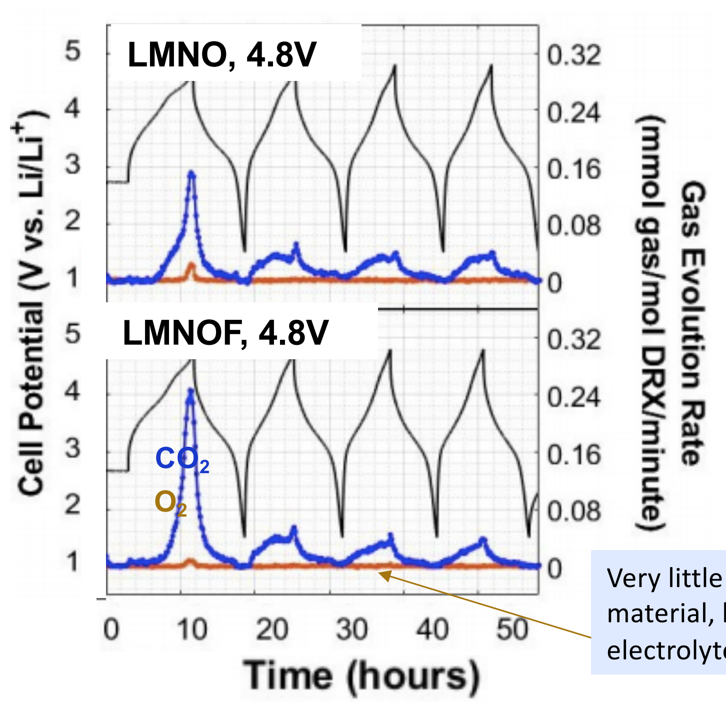

- $^{19}F$ NMR indicates no LiF phase formation in DRX after 20 charge-discharge cycles.
- $^{7}Li$ NMR reveals presence of $Li_2CO_3$ and/or $Li_2O$ in samples.

# Carbonates on surface during LMNOF cycling

- $CO_3^{2-}$ formation upon discharge, and disappear upon charge
- $CO_3^{2-}$ Continues to persist with cycling
- Continuous $CO_2$ evolution with cycling, indicating possible electrolyte breakdown at TOC



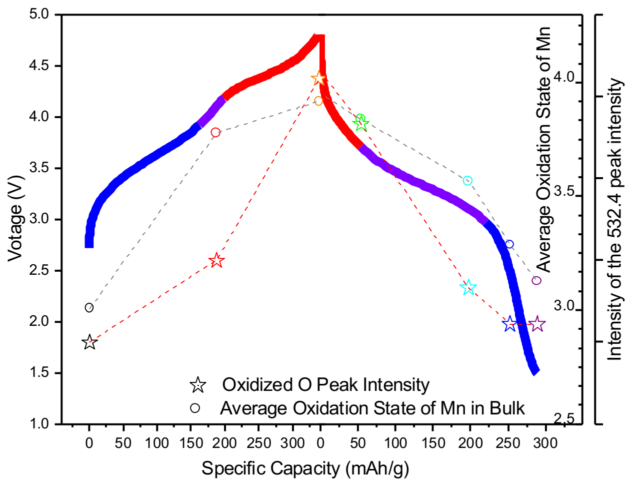

O K-edge XAS for surface
Polyethylene binder, $LiClO_4$ salt



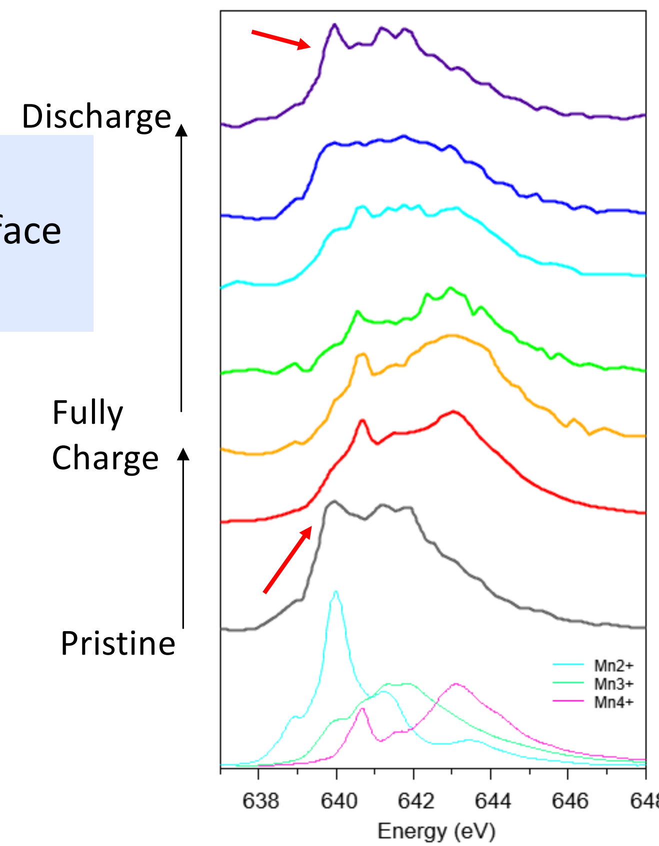

Very little O-loss from Fluorinated material, but CO2 release (from electrolyte)

# Mn redox at the surface of LMNOF characterized with iPFY and TEY

- Surface $Mn^{2+}$ at Discharge
- Reversible oxidation/reduction of surface Mn, even though bulk is $Mn^{3+}/Mn^{4+}$

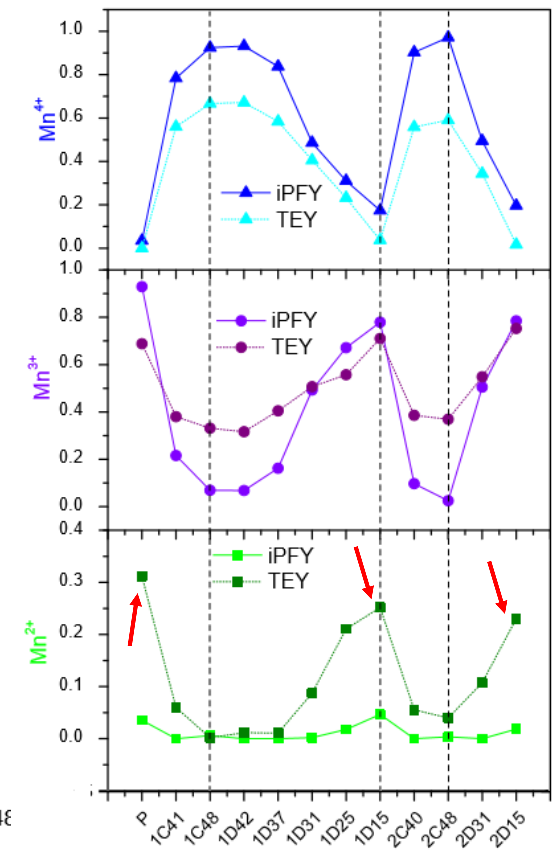



Electrochemical profile for the first cycle



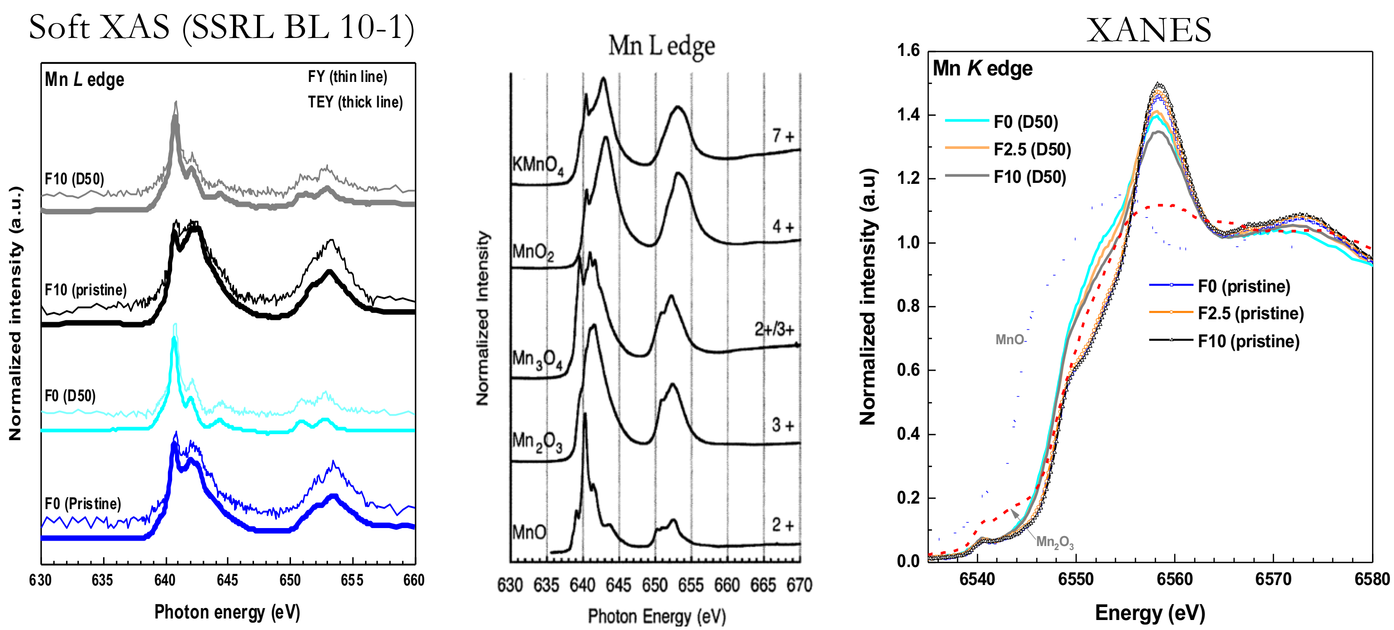

Mn L-edge XAS for the first cycle

TEY – reflect surface signal




Composition of different Mn oxidation state at each stage

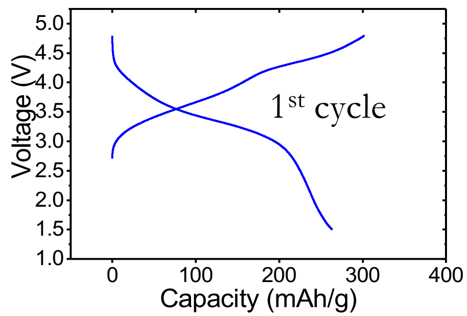
# *Ex situ* X-ray Spectroscopy of DRX Electrodes

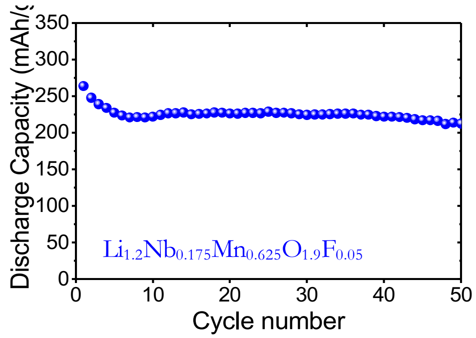



*Gilbert, B., et al., J. Phys. Chem. A., 2003* ***107*** *2839*

- Reduction of $Mn^{(III)}$ to $Mn^{(II)}$ on the surface and in the bulk during cycling
- No effect of fluorine on Mn and O chemical changes during cycling

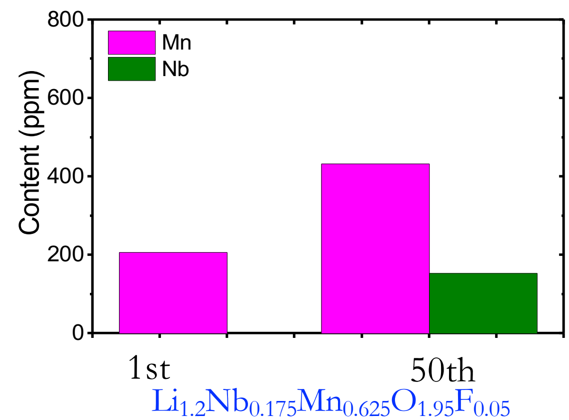
# Very small amount of TM Dissolution in $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$




Any TM loss from DRX does not seem to influence cycling stability

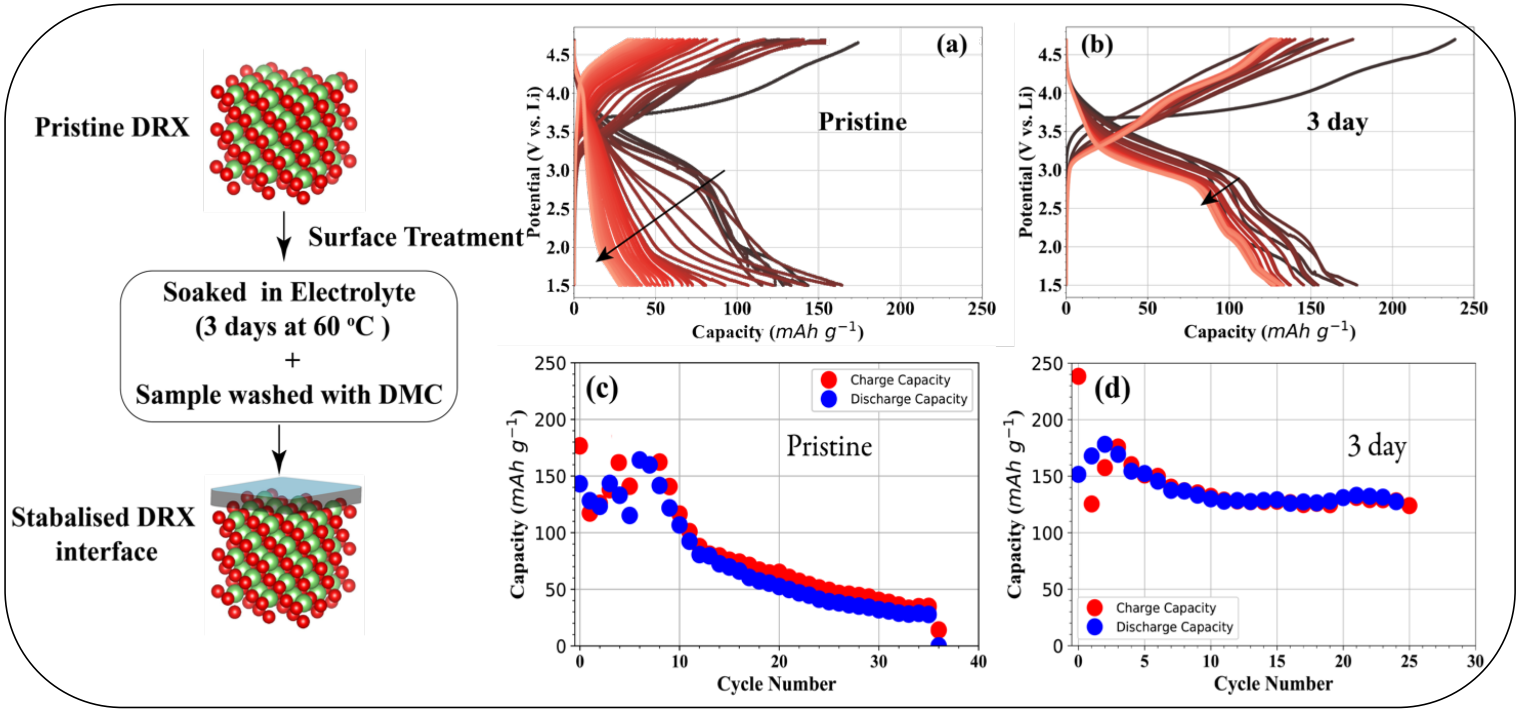
TM content in recovered electrolyte (ICP analysis)




| DRX | Mn/Nb molar ratio in electrode (Pristine cathode) | Mn/Nb molar ratio in electrolyte(After 50 cycles) |
|---|---|---|
| $Li_{1.2}Nb_{0.175}Mn_{0.625}O_{1.9}F_{0.05}$ | 3.57 | 4.76 |

- Small amount of Mn detected in the electrolyte after the 1st cycle
- Non-stoichiometric amount of Mn and Nb detected after 50 cycles.

# Mitigating Capacity/Voltage Fade




- Pre-treatment leads to improvement of electrochemical performance
  - $Mn^{4+/3+}$ redox plateau is retained
  - Sample retains 80 % of its initial discharge capacity
- Carbon coating should improve the performance further

# Conclusions

- 100 and 110 facets dominate surface of F-DRX materials and surfaces are enriched in F.
- LiF exists at the surface of LMNOF, but in small quantities, disappears from surface after ~few cycles. Not clear if dissolves or is covered with electrolyte decomp products.
- Systematic investigation of the F in the electrolyte and cathode surface film indicates that most of it comes from $LiPF_6$ decomposition at high voltage. Very little F loss, if at all, from F-DRX
- $Mn^{2+}$ exists on surface in pristine material
  - $Mn^{2+}$ exhibits reversible redox with cycling
  - Computational insights on Mn binding suggest Mn-F interactions increase binding energy
- Very little $O_2$ evolution from DRX and F-DRX but repeated formation of carbonates and evolution of $CO_2$ indicates electrolyte solvent breakdown to $Li_2CO_3$ and $Li_2O$.
- Small amount of TM loss observed with cycling. No effect on capacity in half cell.
- No LiF phase formation in the bulk of the F-DRX with cycling
- Surface treatment appears as a viable technique to impede the high voltage fade

# Future Work

- Characterize surface structure and chemical composition of DRX materials before and after cycling
- Deconvolute the mechanism of the electrochemical performance degradation of composite DRX cathodes: surface vs. bulk effects; role of the passive components. To what extent is capacity loss due to impedance growth on surface ?
- Better understand the role of fluorine on the interfacial stability of F-DRX materials
- Correlate the effect of DRX surface pretreatment with the physico-chemical properties of the composite cathode
- Investigate alternative electrolytes to $LiPF_6$ in EC/DEC

*"Any proposed future work is subject to changes based on funding levels."*

# Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

# Contributors and Collaborators

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# Remaining Challenges and Barriers

- DRX cycling stability at high voltages
  - We need to better understand whether fade issues at high voltage is intrinsic to DRX material or related to detrimental electrode/electrolyte interactions, similar to what occurs on layered oxide cathodes?
  - Need to understand reactivity with other potential salts and electrolytes
- DRX rate capability
  - While we understand the relation between ionic conductivity and structure and have been able significantly improve Li-ion transport, electronic conductivity of some DRX materials is low. We need to understand better how good electrodes can be made with such materials without using too much carbon (e.g. lessons learned from LiFePO4)
- Subtle changes in surface and bulk structure may affect performance over time, but this is not clear yet.
- Need to further investigate the use of other F sources (e.g. not LiF) to achieve potential higher F incorporation rates for further performance improvement

# Summary

- Characterized in detail the bulk and surface structure of DRX materials, the electrochemical processes, and any changes in structure upon cycling
- Short-range cation order (SRO) has a significant effect of Li-ion mobility and therefore on rate capability. We developed techniques to characterize SRO and identified the three types of SRO and their effect on performance. By modifying SRO, we were able to significantly improve the rate capability, achieving charge/discharge of up to 2A/g
- Fluorinated materials have good stability and cycle life. All DRX materials have low oxygen loss at high voltage, but F-materials have minimal oxygen loss. Small amounts of F reduces Li transport (even though it improves cycle life), but larger amounts of F improve Li percolation and rate.
- We established the F solubility limits for multiple DRX compounds in solid-state synthesis and are evaluating whether this can be increased through the use of other precursors.
- Most DRX compounds have some O-redox, as quantified with RIXS, but in some cases this O-redox is limited to the bulk and appears to be reversible.
- Some changes in the bulk take place when cycling high Mn-content compounds, but they do not seem to negatively impact capacity.
- High voltage charging causes surface reactions with electrolyte, and possibly surface of DRX, but this needs further investigation.